

REACTIVITY OF DOUBLY-CONJUGATED KETONES

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THE REACTIVITY OF DOUBLY-CONJUGATED KETONES.

A THESIS

by

ROSE MAY DAVIS.

Presented in part fulfilment of
the requirements for the Degree of
Master of Arts at Duke University.

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Durham, N.C.

May, 1926.

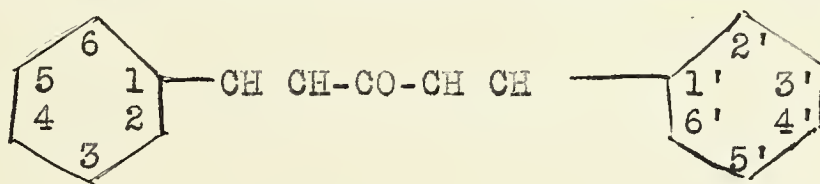
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NOMENCLATURE.

The compounds discussed herein are named on the system which takes dibenzalacetone as the reference compound. For the present purpose the systematic name Distyryl Ketone is used and the numbering is as follows:-



Occasionally the old system, based on the names of aldehydes required to produce the ketone, is used. Thus, distyryl ketone is also named dibenzalacetone.

For brevity, 4'-dimethylamino-2-hydroxydistyryl ketone is frequently referred to as the "orthohydroxy ketone" and 4'-dimethylamino-4-hydroxydistyryl ketone as the "parahydroxy ketone".

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REACTIVITY OF DOUBLY-CONJUGATED KETONES

4'-DIMETHYLAMINO-4-HYDROXYDISTYRYL KETONE.

The subject under discussion is one of great extent and complexity so that it will be necessary at the outset to limit it to one particular aspect.

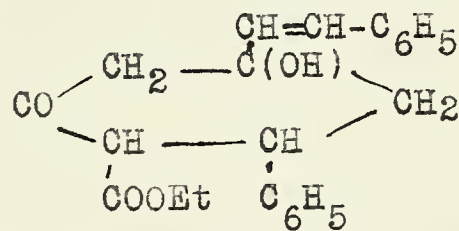
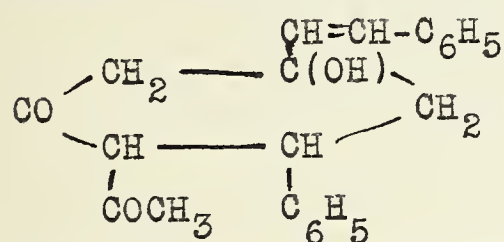
Ever since the introduction of Johannes Thiele's theory in 1899, the subject of "crossed double bonds" (Gekreuzte konjugierte Doppelbindungen) has excited considerable interest. The subject is more clearly understandable if valency, or free affinity is regarded as signless, that is, of the type of gravitation. If we consider a single ethylene bond, >A=A< the valency force between the atoms A is not twice that of a single bond, so that there remains on the atoms A a certain amount of residual affinity, which is regarded as initiating the addition reactions characteristic of this bond. The energy is latent and only called into actual being in the presence of another molecule which itself possesses latent residual valency (eg. ethylene with bromine). If now we take two double bonds on 1:3 atoms, >A=A-A=A< and apply the foregoing considerations, it is clear that all four atoms would develop residual affinity >A=A-A=A< Under these circumstances the affinity of the two central atoms becomes self-neutralised, or, in other words, it fails to

In the foregoing argument, it has been assumed that the six atoms A are identical. If this be not so, then the relative free affinity of the atoms will be altered, but in the main will be substantially the same, occurring chiefly on A1, A5, A6 with practically none on A3 and an indefinite amount on A2 and A4. This is well shown by the system $\begin{matrix} 1 & 2 & 3 & 4 & 5 \\ >C=C-C-C=O \\ & & || \\ & & C_6 \end{matrix}$ where bromine adds chiefly at atoms 1 and 6 but also at 1 and 2. (Dibenzal-propionic acid - An. 306, 115) - $C_6H_5-CH=CH-C(COOH)=CH-C_6H_5$ gives $C_6H_5CHBr-CH=C(COOH)-CHBr-C_6H_5$ and some $C_6H_5-CHBr-CHBr-C(COOH)=CH-C_6H_5$ The example is not very good since it involves a carboxyl group which does not possess great residual valency.

One of the best systems for study is that of the distyryl ketones $\begin{matrix} 1 & 2 & 3 & 4 & 5 \\ R-CH=CH-C-CH=CH-R' \\ & & || \\ & & O \end{matrix}$ where the carbonyl group possesses considerable free energy. Since the distyryl ketones differ only in the nature of the radicles R and R' (substituted or bare benzene rings) it follows that all differences of reactivity between the members of this group must be attributed to the influence of the groups R and R' on the valency relation of the crossed double bond system. That such differences do exist is proved by the fact (Borsche An. 1910, 375, 145) that distyryl ketone itself readily adds on acetylacetone or acetoacetic ester, giving respectively

2-acetyl-3-phenyl-5-styrylcyclohexan-5-ol-1-one and

Ethyl 3-phenyl-5-styrylcyclohexan-5-ol-1-one-2-carboxylate



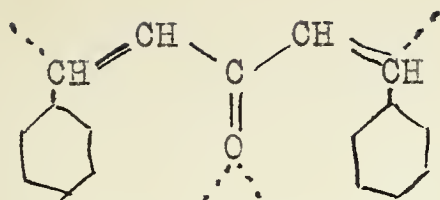
while pp'-tetramethyldiaminodistyryl ketone will not add on these reagents. Similarly pp'-dimethoxydistyryl ketone and dicinnamal acetone also refuse to react, while compounds like p-dimethylaminodistyryl ketone react with difficulty.

Borsche therefore assumes that there exists some form of intramolecular neutralisation in the case of the inactive compounds. When the benzene ring is substituted, it is the substituent which is assumed to absorb the partial valency of the atoms 1 and 5. Thus with pp'-tetramethyl-

diaminodistyryl ketone, the neutralisation process would be represented $\text{NMe}_2\text{C}_6\text{H}_4, \text{CH}=\text{CH}-\text{C}-\text{CH}=\text{CH}-\text{C}_6\text{H}_4, \text{NMe}_2$, the broken

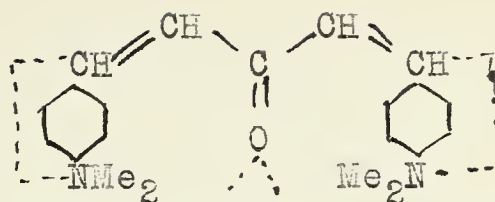
line being taken literally or figuratively to represent some process taking place through the ring. This is conceivable in the case of highly unsaturated NMe₂ groups but is not so easy to accept in the case of weakly unsaturated OMe groups. In addition, the explanations given for the cases of dianisalacetone and benzalanisalacetone involve still further assumptions, thus in the former case the carbonyloxygen is involved, in the latter, the ortho position on one ring. Diagrammatically, the formulae are:-

(1)



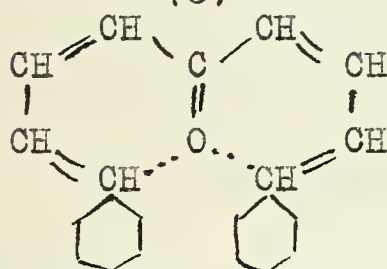
Distyryl ketone

(2)



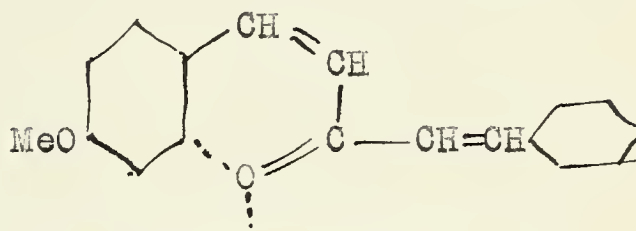
p-p'-tetramethyldiaminodistyryl ketone

(3)



Dicinnamal acetone

(4)



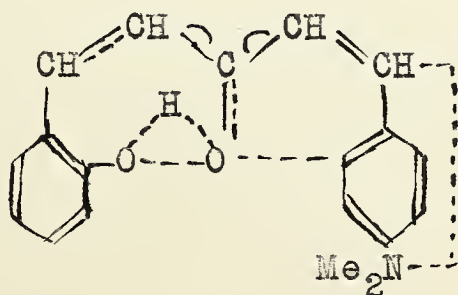
p-methoxydistyryl ketone

It will be seen that formulae 1 and 2 imply equal activity of the carbonyl groups and that formula 3 implies that the carbonyl group is inactive. From some unpublished work of J. S. Buck this is far from true (see note at end). Also, from Borsche's formulae it is clear that only para substitution would be expected to have any marked effect on the reactivity.

Heilbron and Buck undertook to examine the case where an ortho group was introduced into one ring, a para group being present in the other ring. To make the test more crucial the ortho group was hydroxyl (acidic) and the para group dimethylamino (basic). The 4'-dimethylamino-2-hydroxydistyryl ketone so obtained proved to possess extraordinary properties. It readily condensed with ethylacetoacetate (Heilbron, Forster & Whitworth, J.C.S., 1925, 127, 2159) thus forcing one to assume, if Borsche's argument is valid, that the orthohydroxyl group has an activating effect (compare p-dimethylaminodistyryl ketone). The most extraordinary property of the compound, however, was its great additive power, not in the sense of grosser additions where actual condensation takes place, but

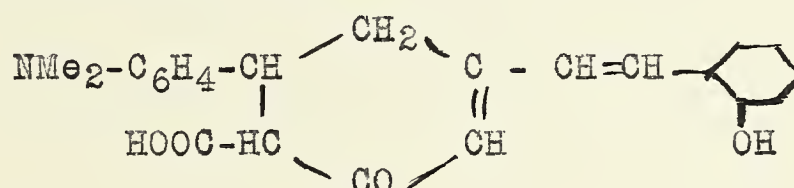
in respect to inactive molecules, such as benzene, alcohol, etc., with which it formed stable addition products. In fact, only naphthalene, anthracene and strangely enough sym-trinitroanisoie were found not to combine.

Clearly then, the hydroxyl group, in conjunction with the dimethylamino group has some profoundly disturbing effect on the molecule, whereby an excessive amount of free valency becomes localised at one point. The hydroxyl and dimethylamino groups alone do not produce this effect (as witnessed by 22'dihydroxy-distyryl ketone and 44'tetramethyldiaminodistyryl ketone which do not exhibit any additive properties, nor do they add on acetoacetic ester). Evidence to the same effect is furnished by the fact that, on modifying the hydroxyl group by methylation, the resulting methyl ether only shows very feeble additive properties. Hence, Heilbron & Buck, J.C.S., 1921, 119, 1500 were led to postulate the existence of a complex group formed by the hydroxyl and carbonyl groups. Such a formation would, if Borsche's ideas as expressed in formulae I and II be retained, result in a marked concentration of the free valency of the compound on the carbon atom I. It is reasonable also to assume a partial bond between the carbonyl group and the ortho position of the right-hand benzene ring. The formula would then appear as



It will be seen that the partial valencies assumed all conjugate exactly with the other bonds.

Two objections may be urged against this. One is the formation of a seven or eight member heterocyclic ring. Spatially it is very probable that the group $\overset{H}{O}-O$ would approximate to a carbon atom; at any rate, since full bonds are not exclusively involved, there is no precedent against it. Very similar types of complex formation have been assumed for many nitrophenols etc. Secondly, in the paper by Heilbron etc., (loc. cit.) ethyl acetoacetate condenses with the ketone to form Ethyl-3-p-dimethylaminophenyl-5-O-hydroxystyryl-⁵-cyclohexen-1-one-2-carboxylate,



the structure of which was proved by oxidation to salicylic acid. This would seem to imply that the partial valency was more intense on the right half of the molecule. A closer examination will show that this is not correct since the primary action of acetoacetic ester is the attack of the CO group; once this is affected, the foregoing considerations do not hold, or at any rate, hold only partially.

This thesis work was undertaken in order to test several important points in connection with the reactivity of the

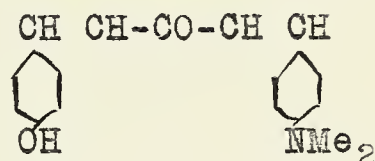
distyryl ketones. The first question which arose was whether other distyryl ketones possessed additive powers which might have been overlooked. A number of typical ketones was examined, but apart from picric and salicylic acids, which generally formed unstable, indefinite compounds, no addition compounds were found. The criterion of formation was the stability to recrystallisation. There is very probably formed, in a number of cases, unstable addition compounds but if the solvent be increased, these dissociate. They are also decomposed on washing with solvent and hence were not examined. It is interesting to note that when the ketones are "streaked" with many substances, very dark colors are produced, indicating compound formation in the solid state.

The second important point to decide was whether the hydroxyl and dimethylamino groups per se were responsible for the additive properties and not the formation of a valency ring. A ketone, the subject of this paper, was prepared, wherein both the hydroxyl and dimethylamino groups occupied para positions. It exhibited no additive properties, and thus proved that the hydroxyl group in the ortho position, and only in the ortho position, in conjunction with the para dimethylamino group was responsible for the intense additivity, this being therefore a function of position. Evidence of another nature is shown by the comparatively ready formation of hydroxylamine and semicarbazide derivatives of the orthohydroxy ketone, while the parahydroxy ketone does not

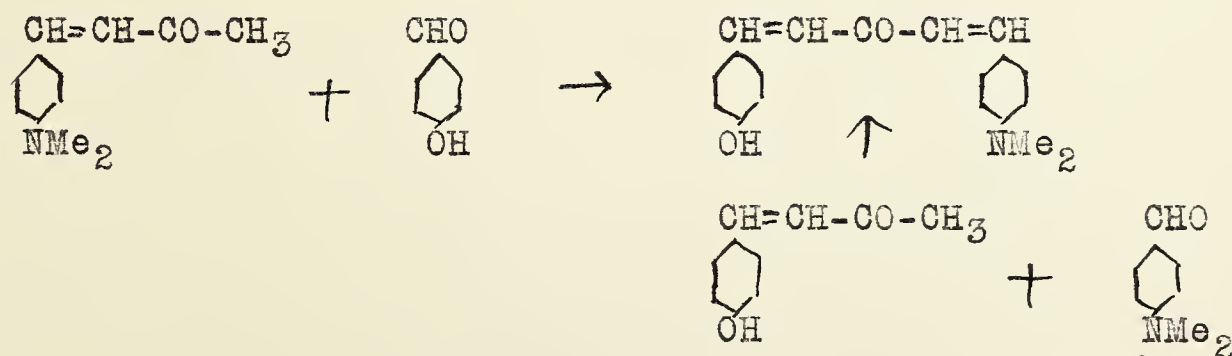
give definite derivatives with either reagent.

A third question, yet to be examined, is the addition of acetoacetic ester. This, if possible, will be carried out and should furnish valuable information.

The production of the ketone
was accompanied by several difficulties.



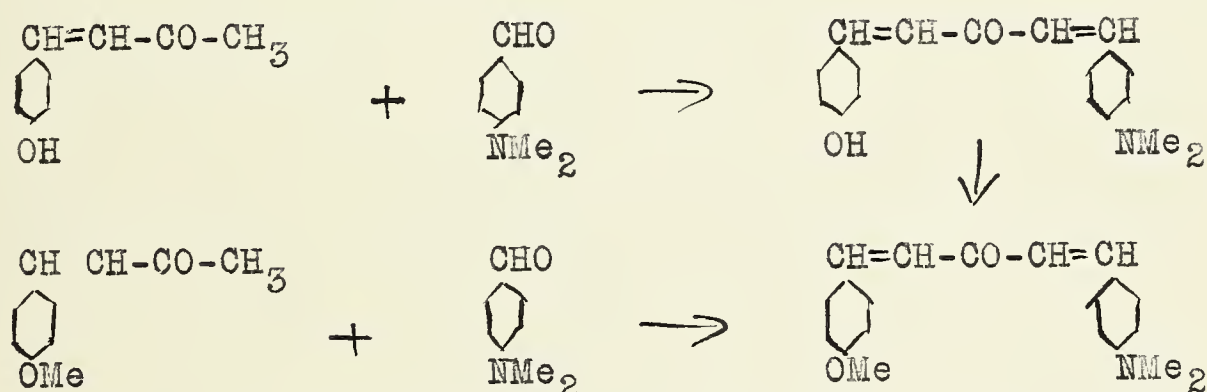
Acid condensations (hydrogen chloride in water, alcohol and acetic acid) failed to yield any but amorphous or tarry compounds. No comparison with the orthohydroxy ketone could be made in this direction on account of the formation of benzopyrylium compounds by ring closure after the usual manner (Heilbron and Buck). It was therefore necessary to resort to alkaline condensations of the type used to produce the orthohydroxy ketone. At the outset considerable difficulty was anticipated and this expectation was realised. Two methods only were available (1) the condensation of p-dimethylamino-styryl methyl ketone with p-hydroxybenzaldehyde and (2) the condensation of p-hydroxy-styryl methyl ketone with p-dimethylamino-benzaldehyde.



The first method had failed in the case of ortho-hydroxy ketone and it also failed in the present case. Heilbron and Buck, in spite of many efforts, had failed to condense p-hydroxystyryl methyl ketone with salicylaldehyde, etc., the products apparently forming and at once breaking up. In the present case, the writer has succeeded in preparing 4'-dimethyl-amino-4-hydroxydistyryl ketone, although only in poor yield and always accompanied by much pp'-tetramethyldiamino distyryl ketone. Indeed, using method I, this latter was the only product isolated. A peculiarity which caused great difficulty and which is not yet completely overcome, is that the alkali salt of the parahydroxy ketone is soluble in water and not easily hydrolysed (the contrary being the case with the ortho-hydroxy ketone) so that it is necessary to neutralise the reaction mixture, obtaining thus the ketone mixed with the tetramethyl derivative. It is a matter of extreme difficulty to separate these two, as the solubility is practically the same and a phenomenon akin to coprecipitation takes place. Several of the derivatives behave similarly. The analysis of these compounds was also a matter of difficulty. Using excess of oxygen throughout, good values were obtained, but it was impossible to burn the compounds without small explosions, probably due to methane. The methyl ether was particularly difficult in these respect. Nitrogen determinations were exceedingly difficult and of doubtful value (by the Dumas method) probably due again to methane evolution (a phenomenon

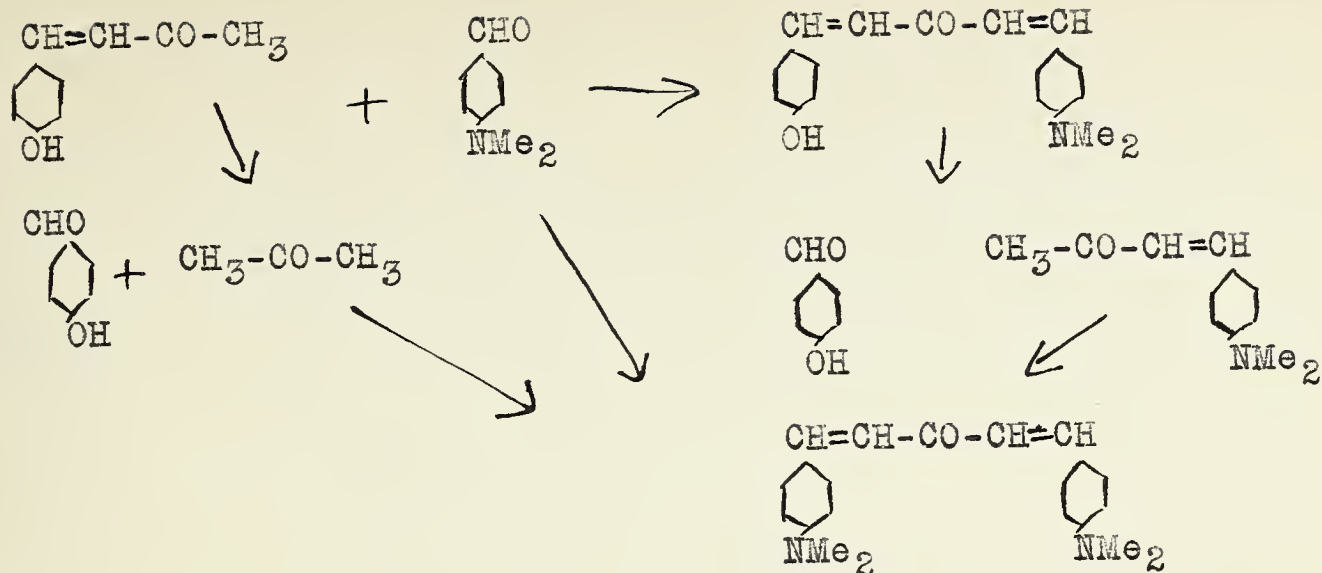
of not infrequent occurrence), but possibly due to small amounts of the tetramethyl ketone which does not seriously affect carbon-hydrogen analyses.

To verify the structure of the para hydroxy ketone it was methylated, and the product compared with the methyl ether prepared from p'-dimethylaminobenzaldehyde and p-methoxystyryl methyl ketone. They were identical.



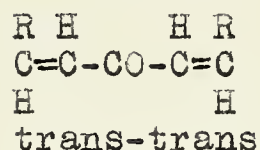
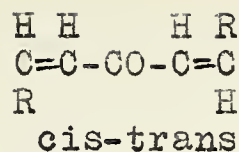
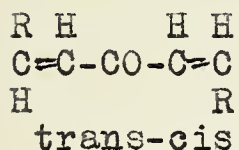
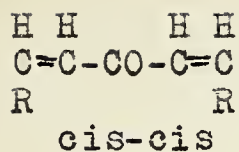
In the direct preparation of the methyl ether only small yields were obtained, much gummy matter being produced. This is in conformity with the observations of Heilbron and Buck who failed to obtain anything but oils by condensing o-methoxy styryl methyl ketone with p-dimethylaminobenzaldehyde.

It is evident that in the condensation of a styryl methyl ketone and an aldehyde a sort of mass action effect rules. In short, during the formation of the distyryl ketone the styryl-methyl ketone is continually breaking up, while the product also breaks up, the formation of other derivatives from these fragments taking place simultaneously and the less soluble or more stable compound finally preponderating. This phenomenon accounts for the production of the tetramethyl ketone.



The failure of the acid condensation is not surprising for obviously it is the hydrochloride of the aminoaldehyde and not the aldehyde itself which reacts - a quite different matter. Also halochromy plays an important role and must profoundly modify the reactivity. That it plays a part in the present case is evident from the intense red color of the reaction mixture. Even when no amino group is present (pp'dimethoxydistyryl ketone) halochromy plays a role, the feebly basic methoxyl groups functioning basically. When no basic group is present (pp'dihydroxydistyryl ketone) the reaction goes smoothly, but nevertheless halochromy (necessarily on the double bonds) is present.

An important aspect of the question of the reactivity of the distyryl ketones is the problem of the configuration. This possibility seems to have been entirely overlooked hitherto. In the case of a symmetrical distyryl ketone evidently there are three possibilities, cis-cis (all refer to H) cis-trans, trans-cis and trans-trans, the second and third being identical. If the ketone is not symmetrical, then the second and third are not the same and four isomers are possible.



Several cases of isomerism, due undoubtedly to the double bond in the styryl methyl ketones are known (Haber, Buck & Heilbron, etc.,) but with the doubtful exception of Zincke & Mulhausen in the case of pp'-dihydroxy-distyryl ketone, no mention has been made of isomers of the distyryl ketones. Buck & Heilbron have noted certain differences in different preparations of the orthohydroxy ketone and ascribed them to different "phases", which amounts to the same as different configurations. It is evident that only a cis-cis ketone can be fully active if the theory advanced holds, since no other configuration allows of the formation of two valency rings. On the other hand, the cis-trans form would show some additivity while the trans-cis would show little and the trans-trans none. The orthohydroxy ketone has been obtained in an unstable yellow form and the methyl ether of this ketone in a fairly stable yellow form, so that at least three configurations are indicated - the cis-cis for the reactive form, the cis-trans or trans-cis for the less active form from ethylacetate-heptane, and the trans-trans for the yellow unstable form, since here the valency fields are in the least condensed condition and the

color would be least intense.

In the parahydroxy ketone, the methyl ether is orange yellow, the ketone bright red, whereas precedent would indicate the contrary. Evidently the configuration is different. Solutions of the ketone, when not too concentrated (eg. in benzene) exhibit a pale yellow color.


It is evident therefore that much remains to be done in this field and much also in the field of halochromy. It is easily possible that if cis-cis forms of other ketones of this series could be obtained, they would exhibit marked additivity. Even the tetramethyl ketone would then be active. The writer has made several attempts to isolate other forms of, eg., 4'-methoxy-2-hydroxydistyryl ketone by boiling the usual yellow form with water. A green very soluble product is formed after several hours, but it has not been possible to purify this. Another observation of the same order is that on acidifying an alkaline solution, the ketone separates as an orange red gum which slowly changed to bright yellow solid. Crystallisation of the ketone from acetoacetic ester (a method which in other cases proved to be effective) had no effect. It seems highly desirable that further work be done on this problem but it will be extremely difficult.

Concurrently with the foregoing work, there was carried out in this laboratory for another purpose, an investigation

of the action of hydroxylamine on certain distyryl ketone. Apart from the production of eight different derivatives of distyryl ketone itself and an oximino-oxime of 2,2'-dihydroxydistyryl ketone, no work has been published on this subject with the exception of that on the 2-hydroxy ketone (Heilbron & Buck) and its methyl ether. These are peculiar in many ways and the fairly easy isolation of derivatives is to be ascribed to the existence of a stable, highly unsymmetrical configuration, the oxime group being as it were, thus forced into one position preferentially. If one considers an unsymmetrical ketone such as 4'-methoxy-2-hydroxydistyryl ketone, with no marked directive force and capable of existing in four forms and takes into account also the various derivatives in their respective α and β forms (such as oxime, oximino-oxime, oximino-oxime oxide, dioximino-oxime) a large number (probably over one hundred) of compounds is possible. As a matter of fact, highly complex mixtures were obtained, from which only rarely could crystalline material be obtained, and this, when obtained, shifted its melting point, indicating transitions. This investigation, having failed in its chief object, the obtaining of normal oximes was abandoned.

Were it possible to overcome experimental difficulties, it would be an elegant method for investigating the crossed double bond system, as hydroxylamine adds easily with the carbonyl group. Different distyryl ketones would thus give

different derivatives and the position of the oximino groups could be easily fixed, thus indicating which bonds were more active and also indicating the comparative activity of the carbonyl group. Comparison of a series of differently substituted styryl groups would throw much light on benzene substitution, from an entirely new angle.

It has been tacitly assumed that the valency of carbon is capable of existing in less than whole units. This is in effect Werner's hypothesis and it seems necessary and acceptable and has been used by many writers and is implied by Thiele. For example, in $\text{>C=C}_\text{C}=\text{C}<$ clearly the curved bond indicates valency less than one unit and greater than zero and consequently the double bonds must in reality be less than two valencies. In this paper they have therefore been represented , the broken line indicating an amount of valency between one and zero. The modern electron theory of Lewis and Langmuir seems powerless to explain subtle additions since neither covalence nor electrovalence is involved. The partial valency theory is admittedly vague but far less so than a nebulous "field" which is all that the electron hypothesis can offer.

Note on Halochromy.

The term halochromy has been several times used in the foregoing discussion. A few words of explanation will therefore not be amiss. In 1884, Claisen and Ponder observed that certain organic compounds were capable of developing more or less deep colors in the presence of certain acids or salts, this phenomenon being shown by compounds which did not possess a basic group as ordinarily understood (such as NH_2)

The subject was then taken up by V. Baeyer, who gave the name "halochromy" (salt colors) and the work was continued by Vorlaender, Straus, Pfeiffer, Stobbe, Kehrman and others. A great number of halochromic compounds were prepared and examined, some in the solid state. As a rule a carbonyl group was present, although this is not essential. Ethylene bonds and methoxyl groups also appear to favor halochromy. The compounds are usually yellow or red (the colors seen in Friedel-Craft reactions are halochromic)

Typical examples of halochromic compounds are the double compound of two molecules of dibenzalacetone with chloroplatinic acid (orange) and of the same ketone with mercuric chloride, ferric chloride, etc. Dianisal acetone forms a green compound with three molecules of sulfuric acid, a red one with two molecules and a yellow one with one molecule.

Other examples are the red compounds of alcohols with antimony pentachloride, which reagent also combines with acetic

acid and phenyl acetic acid. Hydroferrocyanic acid forms a long series of compounds with ketones such as acetone, menthone, carone, suberone and camphor. Stannic chloride combines with many aldehydes, benzaldehyde being typical $2C_6H_5CHO.SnCl_4$.

Examples of halochromy might be multiplied almost indefinitely, but this would serve no purpose. As is usual when a phenomenon is obscure, there are a number of explanations advanced. Baeyer favored the view that the addendum was attached to the "basic" methocyl group when possible, Pfeiffer attributes halochromy to the carbonyl group, Kehrman invokes sexavalent carbon and others regard a double bond as being the determining factor. No single explanation appears to fit the facts.

There are many double compounds that are in no wise halochromic, according to accepted ideas and yet which are obviously of a similar type, such as the quinhydrone, the picrates of various hydrocarbons and the addition products of 4'-dimethylamino-2-hydroxydistyryl ketone referred to in this thesis. The inorganic field offers many examples of compounds which could justly be called halochromic, such as $PbS.PbCl_2$, $3PbS.PbCl_2$, $AsAg_3$, $3AgNO_3$, KI_3 , $CsBr_5$, $PbCl_4.2NH_4Cl$, etc.

It would seem that all that can be said of halochromy, with any certainty, is that it is a residual valency phenomenon. Holleman goes even further and states that the color is "probably produced by intramolecular rearrangements of an obscure type" and this statement about summarises our theoretical knowledge of the subject.

EXPERIMENTAL.

Introduction.

General Discussion. As stated in a previous part of this paper, 4'-dimethylamino-4-hydroxydistyryl ketone was produced only after much difficulty and then in poor yield.

The acid condensations were failures as the following results will show. An alcoholic solution containing 16.2 g. (1 mol.) of p-hydroxystyryl methyl ketone and 14.9 g. (1 mol.) p-dimethylaminobenzaldehyde was treated with hydrogen chloride. The resulting dark red solution was kept at room temperature for two days, at the end of which time it had become thick and brownish-red in color, and then diluted to 1000 c.c. with water. The solution at this point became distinctly green. After neutralizing with ten per cent sodium hydroxide solution and solid sodium bicarbonate, a dark brown, tarry product separated leaving a cherry-pink filtrate. It was impossible to obtain any definite compound from the product.

Four g. (1 mol.) of p-dimethylaminobenzaldehyde and 4.4 g. (1 mol.) p-hydroxystyryl methyl ketone were dissolved in 100 c.c. of aqueous hydrogen chloride and the resulting dark red solution was warmed. As the solution cooled, a product began immediately to separate. At the end of one day, a reddish-black, gummy mass was formed, from which no definite compound could be isolated.

4.96 g. (1 mol.) of p-dimethylaminobenzaldehyde and 5.4 g. (1 mol.) of p-hydroxystyryl methyl ketone were dissolved in 100 c.c. of acetic acid and the resulting deep red solution was treated with gaseous hydrogen chloride. The solution was kept at room temperature for two or three days, at the end of which time an amorphous blackish-red tar was produced.

Having been unsuccessful in the attempts at acid condensations and unable to make any comparison with the 4'-dimethylamino-2-hydroxydistyryl ketone in this respect (due to the formation of benzopyrylium compounds) it was necessary to employ the two following methods of alkaline condensations used for the preparation of the orthohydroxy ketone.

Ten g. (1 mol.) of p-dimethylaminostyryl methyl ketone and 7 g. (1 mol.) of p-hydroxybenzaldehyde were dissolved in 130 c.c. of warm alcohol and 4.8 g. (1.5 mol.) of potassium hydroxide in methyl alcohol were added. On the addition of the potassium hydroxide a reddish-orange product separated almost immediately; which upon examination proved to be tetramethyldiaminodistyryl ketone. When the filtrate from the above residue was diluted to 1000 c.c. with water, a voluminous product, which decreased with stirring, formed. After crystallization from alcohol this latter product was found to be p-dimethylaminostyryl methyl ketone. As was expected, the above method failed, as it failed in the case

of orthohydroxy-para-dimethylaminodistyryl ketone, the failure being due, probably, to the immediately breaking up of the products upon formation.

16.2 g. (1 mol.) of p-hydroxystyryl methyl ketone were dissolved in 80 c.c. of warm ten per cent sodium hydroxide solution (2 mols. NaOH) and 14.9 g. (1 mol.) of p'dimethylaminobenzaldehyde, dissolved in 100 c.c. of warm alcohol were added. The deep-red solution which was slightly warmed in order to dissolve the sodium salt which had formed, was kept at room temperature for three days, then diluted to 2000 c.c. with water. Not until solid sodium bicarbonate was added did the p-hydroxy-p-dimethylaminodistyryl ketone begin to separate, and then in a very gummy condition. From five of the above condensations, the total crude yield was 158 g., which upon recrystallization from alcohol, was reduced to 36.4 g.

16.2 g. (1 mol.) of p-hydroxystyryl methyl ketone and 26.1 (1.75 mols) of p-dimethylaminobenzaldehyde were dissolved in 200 c.c. of alcohol and the resulting solution treated with 80 c.c. of ten per cent sodium hydroxide (2 mols. NaOH). The deep-red solution was kept at room temperature for four days and then diluted to 2000 c.c. with water and filtered. On treating the filtered solution with carbon dioxide gas, a tarry mass separated, the terra cotta colored ketone forming a thin layer on the sides and bottom of the

containing vessel.

It is interesting to note that a specimen of the crude ketone resulting from one condensation was quite different from the others in respect to color, form and melting point. Upon filtering, the ketone formed in three layers; the top and bottom layers were compact and of a dull red color, while the center layer consisted of thin, reddish-black glistening flakes. The melting point was 110 C, whereas the crude ketone from the other preparations melted at 185 C. Even after recrystallization from alcohol the ketone displayed the same triple layer formation, but to a less degree.

After considerable experimentation, it was found that a better yield of 4'-dimethylamino-4-hydroxydistyryl ketone was obtained by using 16.2 g. (1 mol.) of p-hydroxystyryl methyl ketone and 26.1 g. (1.75 mols.) of p-dimethylamino-benzaldehyde than by any other proportions of these constituents; however, the yield was always low and accompanied by much p-p'-tetramethyldiaminodistyryl ketone.

The poor yield of the 4'-dimethylamino-4-hydroxydistyryl ketone is obviously due to the presence of the p-p'-tetramethyldiaminodistyryl ketone, the production of which latter compound is in turn due to the fact that in the condensation of p-hydroxystyryl methyl ketone and p-dimethylaminobenzaldehyde (during the formation of 4'-dimethylamino-4-hydroxydistyryl ketone) the p-hydroxystyryl methyl ketone is continually breaking up, while the 4'-dimethylamino-4-hydroxydistyryl

ketone also breaks up (see previous explanation with equations). From these fragments other derivatives form simultaneously, and, of these compounds, the less soluble and more stable p-p'-tetramethyldiaminodistyryl ketone preponderates.

The condition which is responsible for the above result is occasioned by the fact that the alkali salt of 4'-dimethyl-amino-4-hydroxydistyryl ketone is soluble in water and not easily hydrolyzed, this necessitating the neutralization of the reaction mixture, consequently obtaining the tetramethyl derivative mixed with the desired p-hydroxy ketone.

It was exceedingly difficult to obtain the 4'-dimethylamino-4-hydroxydistyryl ketone free from the tetramethyl ketone (the reasons for which have been previously mentioned), and in order to so obtain a pure specimen it was necessary to recrystallize the crude ketone three times from alcohol, extract it for eight hours with benzene in a Soxhlet apparatus and finally recrystallize twice from alcohol. During the extraction and the several recrystallizations the color of the 4'-dimethylamino-4-hydroxy-distyryl ketone changed from a light terra-cotta to a crimson red.

In order to isolate and identify the p-p'-tetramethyl-diaminodistyryl ketone, the liquor from the benzene extractions was evaporated and then treated with petrol ether. The petrol ether and dissolved oil was filtered and evaporated, the residue appearing as orange leaves after recrystallizing twice from alcohol. The compound was identified as p-p'-tetramethyl-

diaminodistyryl ketone by comparison and by the melting point of its mixture with a specimen obtained by Staudinger and Kon's method (A., 1911, 384, 121). The product was further identified as p-p'-tetramethyldiaminodistyryl ketone by comparison of an oxime prepared from the product with an oxime prepared from a specimen of the tetra-methyl ketone (obtained by Staudinger and Kon's method; loc. cit.). The mixed melting point showed no depression.

The additivity of 4'-dimethylamino-4-hydroxydistyryl ketone was examined with respect to the following compounds - m-dinitrobenzene, caffeine, hydro-quinone, quinone, p-dimethylaminobenzaldehyde, picric acid, pyrogalllic acid, phenophthalein, tetra methyl diaminobenzophenone, salicylic acid, vanillin and naphthalene, these being considered a representative selection. The method used consisted of dissolving molecular proportions of each component together in the minimum quantity of hot ethyl alcohol and allowing the solution to crystallize. Modifications were later introduced and varying proportions of the constituents used; however, with the single exception of picric acid no addition compounds were formed.

Other typical ketones such as p-p'-dihydroxydistyryl ketone, 4'-methoxy-2-hydroxydistyryl ketone and p-p'-tetramethyl-diaminodistyryl ketone were examined by the above method, but similarly to the p-hydroxy ketone, no addition products were formed except in the case of picric and salicylic acids

where indefinite complexes were formed.

As stated previously the criterion of addition-compound formation was taken to be the stability to recrystallization. Therefore, unstable compounds which were detected by physical and chemical means but which dissociated when the solvent was increased or which decomposed on washing with the solvent were not further examined.

An interesting example of the above phenomenon was the indefinite addition compound of p-p'-tetramethyldiaminodistyryl ketone and hydroquinone, in which case one molecule of the tetramethyl ketone and five molecules of hydro-quinone were dissolved in the minimum quantity of hot ethyl alcohol, boiled for fifteen minutes and the solution allowed to crystallize. As the solution cooled, fine glistening purple, iridescent crystals appeared, which, however, were stable only in concentrated solution, for when filtered from the mother liquor and treated with cold ethyl alcohol, they began to decompose, the orange-colored tetra methyl ketone being slowly regenerated.

There were indications that addition compounds were formed in the dry state, the evidence being the very dark colors which were produced when the ketones were streaked with different substances.

As far as the production of a definite compound or pure oxime is concerned, the action of hydroxylamine hydrochloride

on 4'-dimethylamino-4-hydroxydistyryl ketone was a failure. An attempt was made to prepare an oxime by the following method (modification of the method of Heilbron & Buck, J.C.S., 1921, 119, 1515.). An alcoholic solution (60 c.c.) containing three g. (1 mol.) of the hydroxylamine hydrochloride and 4 g. (4 mols.) of potassium acetate was heated for two hours and simultaneously treated with carbon dioxide gas to avoid possible oxidation. The solution was then diluted with 800 c.c. of cold water and kept until next day, by which time, only a minute quantity of a light greenish-yellow powder had separated. It was impossible to obtain a definite melting point of this product. Likewise, negative results were obtained when an attempt was made to produce the hydroxylamino-derivative, according to Heilbron & Buck's method (J.C.S., 1921, 119, 1515), in which case one g. (1 mol.) of the para-hydroxy ketone dissolved in 1.37 c.c. of 30 per cent potassium hydroxide solution (4 mols.) was treated with 0.68 g. (3.5 mols.) of hydroxylamine hydrochloride dissolved in 5.5 c.c. of water and 2.5 c.c. of alcohol added to the mixture. The resulting solution was boiled for a few minutes and, although kept for several days, there was no material evidence of a compound formation. The above results are contrary to those obtained from the ortho-hydroxy ketone; which was to be expected from the views previously stated.

Attempts to prepare the hydrochloride of the para-hydroxy ketone, by dissolving one gram of the ketone in 10 c.c. of concentrated hydrochloric acid and warming, were not successful, in that abnormal grayish-brown products of a doubtful composition resulted.

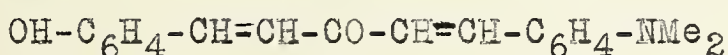
The results, produced by the action of the base, semicarbazide upon the para-hydroxy ketone, were quite as unsuccessful as those obtained in the case of hydroxylamine hydrochloride and in conformity therewith, these results were in opposition to those obtained by the action of the base upon the orthohydroxy ketone. In an effort to obtain a semicarbazide derivative, the following method of Heilbron & Buck (loc. cit.) was employed. Two g. of the para-hydroxy ketone, dissolved in 10 c.c. of pyridine, were mixed with 2.5 g. of semicarbazide hydrochloride dissolved in 7.5 c.c. of water and in order to form a homogeneous solution 7.5 c.c. of alcohol were added. After the mixture was kept for several days, a dull-red precipitate formed, which, upon recrystallization from alcohol, proved to be unchanged ketone.

The action of phenylhydrazine upon the para-hydroxy ketone in the presence of pyridine resulted in the formation of a light apple green product which responded positively to the Knorr pyrazoline reaction, producing a beautiful Gentian violet solution.

The acetyl derivative was prepared according to the method of Heilbron and Buck (loc. cit.) and fairly good results were obtained with the exception of the nitrogen determinations which were somewhat doubtful, probably owing to methane.

The methyl ether was prepared with difficulty by methylation of the parahydroxy ketone in acetone according to Heilbron & Buck's method (loc. cit/). The analysis, as previously stated, was extremely difficult and accompanied by numerous explosions. The methyl derivative was also prepared by direct condensation of p-methoxystyryl methyl ketone with p-dimethylaminobenzaldehyde (which method failed in the case of the ortho-hydroxy ketone) and compared with the above preparation in order to verify the structure of the p-hydroxy ketone.

Condensation for 4'-dimethylamino-
4-hydroxydistyryl ketone.



An alcoholic solution (200 c.c. of alcohol) containing 16.2 g. (1 mol.) of p-hydroxystyryl methyl ketone and 26.1 g. (1.75 mols.) of p-dimethylaminobenzaldehyde was treated with 80 c.c. of ten per cent sodium hydroxide (2 mols. of NaOH). The resulting deep red solution was kept at room temperature for four days and then diluted to 2000 c.c. with water. The diluted solution was kept another day and then filtered.

A tarry mass together with a terra cotta colored product, which gradually separated upon treating the filtrate with carbon dioxide gas (or solid sodium bicarbonate) was filtered off. The substance was purified by repeated recrystallization from absolute alcohol after which it was extracted for eight hours with benzene in a Soxhlet apparatus and then again recrystallized several times from alcohol. The ketone was finally obtained in aggregates of fine crimson-red crystals, softening at 182°C and melting completely at 186°C .

0.1313 g. gave 0.3753 g. CO_2 and .0785 g. H_2O .

.7000 g. gave 29.0 c.c. N_2 at 29°C and 7.57 mm.

Found C=77.9 H=6.7 N=4.54.

$\text{C}_{19}\text{H}_{19}\text{O}_2\text{N}$ requires C=77.8 H=6.5 N=4.78 per cent.

The ketone is slightly soluble in cold alcohol and fairly soluble in hot. In hot chloroform it is moderately soluble and in ether or benzene very sparingly soluble. Nitric acid dissolves the compound giving a reddish amber color, which on dilution gives a clear green solution and a light yellow precipitate. In concentrated sulfuric acid the ketone dissolves with a clear red color which on dilution turns to a dull red color and finally clear yellow green.

When 0.25 g. of the parahydroxy ketone is dissolved in 10 c.c. of concentrated hydrochloric acid and the solution gradually diluted with water, the color phenomena which are observed are in marked contrast to those shown by the ortho-hydroxy ketone (cf. Buck & Heilbron, J.C.S., 1923, 123, 1395).

COLOR REACTIONS.

0.25 g. of ketone dissolved in 10 c.c. of concentrated hydrochloric acid and diluted with water.

<u>Orthohydroxy ketone</u>	<u>Parahydroxy ketone</u>	<u>Volume</u>
Cold solution	Cold solution	
Blood-red	Deep blood-red	10
After ten mins heating	After ten mins heating	
Golden-yellow	Intense blood-red	10
Pale green	Intense blood-red	12
Intense emerald green	Cloudy red-brown	22
Deep bluish-green	Light brown turbidity	30
Deep violet-black	Light brown, green tint	35
Blackish-crimson	Greenish-brown, turbid	40
Deep claret	Light green, turbid	50
Intense red-violet	Light green	75
Intense red-violet	Pale sage-green	150
Pure violet	Clear green	300
Violet-blue	Clear green	600
Deep blue	Yellow-green	1800
Deep royal blue	Light yellow-green	3600
Royal blue	Straw	5×10^5
Distinct blue	Light straw	10^6

The marked difference in behaviour between the two ketones is doubtless due to the non-formation of pyrylium derivatives in the case of the parahydroxy ketone.

Picrate of 4'-dimethylamino-4-hydroxy-
distyryl ketone.

Three grams (1 mol.) of the p-hydroxy ketone and 2.35 g. (1 mol.) of picric acid were dissolved in 70 c.c. of alcohol and heated for a few minutes. The greenish-brown product which immediately commenced to separate, was filtered off after two hours and recrystallised from glacial acetic acid. The compound forms greenish-black crystals with an olive-green streak and melts at 180°-181° C. For analysis it was dried for three weeks over soda-lime.

0.1414 g. gave 0.2954 g. CO₂ and 0.0534 g. H₂O

Found C=57.0 H=4.2 C₁₉H₁₉O₂N.C₆H₃O₇N₃ requires C=57.4 H=4.2 per cent.

The product is slightly soluble in cold ethyl alcohol and moderately soluble in hot alcohol. It is sparingly soluble in ether, benzene and chloroform. The color reactions are similar to those of the parent ketone.

Phenylhydrazine Derivative of
4'-dimethylamino-4-hydroxydistyryl ketone.

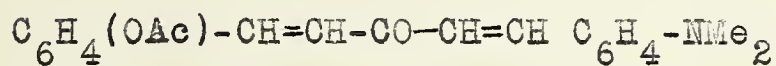
Two grams of the parahydroxy ketone were dissolved in 6 c.c. pyridine and 2.1 g. (3 mols.) phenylhydrazine hydrochloride added. The red-brown solution was then heated on the water-bath for 45 minutes. On adding alcohol a strong yellow-green

fluorescence was apparent. Next day the solid which had separated was filtered off and recrystallised several times from alcohol. It forms light yellow-green bulky masses of slender crystals, shrinking above 120°C and melting at 158°C . It is readily soluble in alcohol, ether, benzene and chloroform, the solutions showing a powerful yellow-green fluorescence. On adding a crystal of potassium nitrate to the orange solution in concentrated sulfuric acid, an intense red-violet color formed. The Knorr pyrazoline reaction was strongly positive. Solutions of the compound in mineral acids have an amber color of various shades.

0.3105 g. gave 29.8 c.c. N_2 at 23°C and 752 mm.

Found $\text{N}=10.7$, $\text{C}_{25}\text{H}_{25}\text{ON}_3$ requires $\text{N}=10.9$ per cent.

Acetyl derivative of 4'-dimethyl-
amino-4-hydroxydistyryl ketone.



Three grams of the p-hydroxy ketone dissolved in 17 c.c. of acetic anhydride, were heated for two hours and the resulting dark red solution was poured into 175 c.c. of cold water. When the dark oil, which settled to the bottom of the green solution was neutralized with 150 c.c. of ten per cent sodium hydroxide solution a dark red crystalline product was precipitated. After recrystallizing three times from alcohol, the compound was obtained in the form of small, deep ochre-colored crystals giving a reddish streak, and melting at 145°. It is slightly soluble in cold ethyl alcohol or ether, fairly soluble in benzene and very soluble in chloroform. The compound dissolves in both concentrated hydrochloric acid and sulphuric acid with a deep reddish-amber color, which becomes pale green on dilution with water. In concentrated nitric acid, it dissolves with a blackish-red color, which becomes green on dilution with water and on further dilution changes to clear yellow.

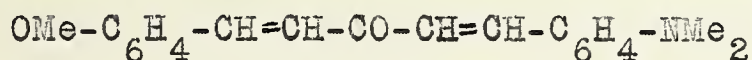
0.1085 g. gave 0.2984 CO₂ and 0.0579 g. H₂O

0.5034 g. gave 23.0 cc/ N₂ at 26° C and 752 mm.

0.5012 g. gave 22.4 c.c. N₂ at 27° C and 752 mm.

Found C=75.0 H=5.93 N=4.92, 5.07. C₂₁ H₂₁ O₃ N requires
C=75.2 H=6.03 N=4.18 per cent.

4'-Dimethylamino-4-methoxydistyryl ketone.



Four and one half g. of the p-hydroxy ketone dissolved in the minimum quantity (45 c.c.) of hot acetone were treated with 16 c.c. of ten per cent sodium hydroxide solution and 4.6 g. (1.5 mols) of dimethyl sulfate added. The resulting mixture was heated for five minutes and then diluted to 200 c.c. with water when brownish-yellow nodules separated. After repeated recrystallisation from alcohol the methyl ether was obtained in two forms, yellow and orange leaves, which give an ochre streak and melt at 140° .

0.1580 g. gave 0.4513 g. CO_2 and 0.0991 g. H_2O

0.5440 g. gave 25.7 c.c. N_2 at 26 and 757 mm.

Found C=77.9 H=6.96 N=5.25

$\text{C}_{20}\text{H}_{21}\text{O}_2\text{N}$ requires C=78.2 H=6.84 N=4.56 per cent.

The compound is slightly soluble in ethyl alcohol, sparingly soluble in ether, moderately soluble in benzene and very soluble in chloroform. It dissolves in concentrated hydrochloric acid with the blood-red color which becomes amber on dilution with water, and on further dilution changes to greenish-yellow. Hydrogen chloride changes the color of the methyl ether to a glistening purplish black. In concentrated nitric acid the substance dissolved with a reddish-brown color and on dilution with water a light green precipitate formed.

The cherry-red color, which was produced when the product dissolved in concentrated sulphuric acid, became amber on dilution with water.

For the preparation of a few of the compounds used in this research, the following methods were employed.

2-Hydroxy styryl methyl ketone.

(Harries, B, 1891, 24, 3180)

Fifty g. of salicylaldehyde, dissolved in 140 g. of ten per cent. sodium hydroxide solution were treated with 50 g. of acetone and a further 200 c.c. of ten per cent sodium hydroxide. The resulting orange-red solution was diluted to 2000 c.c. with water and kept for three days. On precipitation with dilute acetic acid the ketone was obtained as fine yellow crystals. When purification of the ketone was necessary, it was recrystallised from hot benzene instead of being subjected to the steam treatment suggested by Harries. M.P. 139°. Yield (crude) 49.8 g.

4-Hydroxy styryl methyl ketone.

(Buck & Heilbron, J.C.S., 1922, 121, 1100)

Forty g. of p-hydroxybenzaldehyde were dissolved in 150 c.c. of acetone and the solution was treated with 53 c.c. fifty per cent sodium hydroxide solution (2 mols.). After adding 100 c.c. of water, the mixture was gently warmed and kept until the following day, by which time it had solidified to an orange-red crystalline mass. Upon dissolving the product in water and decomposing with dilute acetic acid, a reddish-yellow oil separated out which solidified on standing. The ketone was obtained in the crude form as maroon needles. M.P. 114°-115°. Yield - 46 g.

4-Dimethylamino styryl methyl ketone.

(Sachs & Lewin, B. 1902, 35, 3575)

Twenty g. of p-dimethylaminobenzaldehyde dissolved in 40 c.c. of alcohol were treated with 14.6 c.c. (1.5 mols) of acetone and a few drops of ten per cent sodium hydroxide solution. Upon rubbing, the mixture solidified in a few minutes to an orange crystalline mass. After recrystallizing from alcohol, the ketone was obtained as orange-yellow spears. M.P. 234°-235°. Yield - 15 g.

4-4'-Tetramethyldiamino distyryl ketone.

(Staudinger & Kon, A. 1911, 384, 121)

This ketone was produced by direct condensation of two molecules of p-dimethylamino benzaldehyde and one molecule of acetone. 15 g. of p-dimethylaminobenzaldehyde dissolved in minimum quantity of alcohol, were treated with 3.5 c.c. of acetone and 3 c.c. of ten per cent sodium hydroxide solution and warmed for a few minutes. By the following day the mixture had crystallised to yellow-orange mass. The product recrystallised from alcohol as orange leaves. M.P. 163°-165°. Yield - 10 g.

2-2'-Dihydroxydistyryl ketone.

(Decker & Felser B, 1908, 41, 2997)

Instead of using 2 mols of salicylaldehyde, 1 mol. of acetone, 6 to 8 volumes of alcohol, 3 to 4 mols. of potassium hydroxide in alcohol as directed by Decker & Felser, the constituents were used in the following proportions; Acetic acid being substituted for carbon dioxide.

122 g. (1 mol.) of salicylaldehyde and 29.03 g. (0.5 mol.) of acetone were dissolved in 275 c.c. (1.5 to 2 volumes) of alcohol and treated with 245 c.c. (1.75 volumes) of 40 per cent sodium hydroxide solution. The resulting deep red solution which evolved heat, was cooled and kept until the following day, when a crystalline mass of green iridescent, long dark red needles

had formed. This product was dissolved in 4000 c.c. of water and the ketone precipitated with dilute acetic acid, was obtained as a voluminous mass of fine, bright yellow crystals. M.P. 168°. Yield (crude) - 133 g.

4'-Methoxy-2-hydroxydistyryl ketone.

(Buck & Heilbron, J.C.S., 1922, 121, 1098)

Twenty-four g. of o-hydroxystyryl methyl ketone and 27.2 g. anisaldehyde were dissolved in 140 c.c. of absolute alcohol and the resulting solution was treated with 32 c.c. of 50 per cent sodium hydroxide solution (2 mols. NaOH). Bright red needles of the sodium salt which separated out on standing at room temperature, were suspended in cold water and decomposed with dilute acetic acid. A yellow gummy product separated, which, upon hardening was filtered off. After drying, the ketone formed in tiny brownish-yellow needles. M.P. 139°.

Yield (crude) - 47 g.

When carbon dioxide was substituted for acetic acid, the product was much less gummy.

3'-4'-Methylenedioxy-2-hydroxy distyryl ketone.

(Buck & Heilbron, J.C.S., 1922, 121, 1095)

32.5 g. of o-hydroxystyryl methyl ketone and 29.5 g. of piperonal were dissolved in 500 c.c. of alcohol and treated with 160 c.c. of ten per cent sodium hydroxide solution (2 mols. NaOH). The resulting deep blood-red solution which was kept for thirty hours, was diluted with cold water and then neutralized with dilute acetic acid. A greenish-yellow, slightly gummy product separated, which, after hardening, was filtered off. Upon drying, the ketone was obtained as dull yellow needles. M/P. 170°-171°. Yield (crude) - 56 g.

4'-Dimethylamino-2-hydroxydistyryl ketone plus

p-dimethylaminobenzaldehyde.

(Heilbron & Buck, J.C.S., 1921, 119, 1507)

16 g. (1 mol.) of o-hydroxystyryl methyl ketone and 22 g. (1.5 mols.) of p-dimethylamino-benzaldehyde were dissolved in alcohol and treated with 80 cc. of ten per cent sodium hydroxide (2 mols. of NaOH). The resulting blood-red mixture was kept at room temperature for three

days and then diluted to 4000 c.c. with water, when a brick-red flocculent precipitate gradually separated. Upon filtering, the ketone formed into brick-red prisms, melting at 143°.

Yield (crude) - 27 g.

In order to remove the p-dimethylaminobenzaldehyde, the ketone was heated in chloroform for forty five minutes. On removing the aldehyde, chloroform was added which, however, was not objectionable for the purpose.

Anisal Acetone. (4-Methoxystyryl methyl ketone)

(Baeyer & Villiger, B., 1902, 35, 1191)

Twenty g. of anisaldehyde and 40 g. of acetone were mixed with 1000 c.c. of water and 500 c.c. of alcohol were added to produce a clear solution. After adding 20 g. of ten per cent sodium hydroxide, a yellow turbidity appeared. A voluminous precipitate of light yellow crystals which formed after several hours was allowed to stand until the following day. After recrystallization from methyl alcohol, the product was obtained as long, almost colorless leaves, melting at 72°-74°.

Yield - 13.5 g.

4'-Dimethylamino-4-methoxydistyryl ketone.

13.5 g. of anisal acetone and 11.4 g. of p-dimethylamino-benzaldehyde dissolved in 300 c.c. of alcohol were treated with 30 c.c. of ten per cent sodium hydroxide and 140 c.c. of water. A yellowish-red, glistening solid separated almost immediately. After recrystallizing twice from alcohol, the methoxy ketone was obtained in two forms (yellow and red leaves) which were identical to those produced by the methylation of 4'-dimethylamino-4-hydroxydistyryl ketone. M.P. 135°.

p-Dimethylaminobenzaldoxime.

An alcoholic solution containing 3g. (1 mol.) of p-dimethylamino-benzaldehyde was treated with a filtered mixture of 4.8 g. (3.5 mols.) of hydroxylamine hydrochloride dissolved in the minimum quantity of water and 7.9 g. (4 mols.) of potassium acetate dissolved in smallest amount of alcohol. After heating the resulting solution for a few minutes, it was cooled and the oxime allowed to separate out. Upon recrystallization from warm aqueous alcohol, the oxime was obtained in dark straw-colored glistening crystals. M.P. 145°.

Yield - 1.5 g.

4-4'-Tetramethyldiaminodistyryl ketoxime.

One g. of the tetramethyl ketone 1.6 g. of hydroxylamine hydrochloride and 2.6 g. of potassium acetate were dissolved in the minimum quantity of alcohol and heated for fifteen minutes. After adding cold water to the solution, a yellow product immediately separated. The oxime, upon recrystallization from alcohol was obtained in the following three forms - fine white crystals (soluble in water), tiny medium yellow crystals and dark yellow lumps.

M.P. (more soluble white form) 206° .

M.P. (less soluble yellow form) 208° .

BIBLIOGRAPHY.

- Auwers, B. 1921, 54, (B), 987.
- Auwers & Voss, B. 1900, 42, 4411-4427.
- Baeyer & Villiger, B. 1902, 35, 1190, 3013.
- Borsche, An. 1910, 375, 145-180.
- Buck & Heilbron, J.C.S., 1922, 121, 1095; 1923, 123, 1392.
- Cohen, Organic Chemistry, Part II.
- Decker & Felser, B. 1908, 41, 2997.
- Graebe & Liebermann, B. 1868, 1, 104.
- Harries, B. 1891, 24, 3180.
- Heilbron & Buck, J.C.S., 1921, 119, 1500-1515.
- Heilbron, Forster & Whitworth, J.C.S., 1925, 127, 2159.
- Henrich, Theories of Organic Chemistry.
- Kauffmann, B. 1916, 47, 1324.
- Kauffmann & Burckhardt, B. 1913, 46, 3808.
- Kauffmann & Kieser, B. 1913, 46, 3788.
- Knorr, B. 1893, 26, 101.
- Kurt Meyer, B. 1910, 43, 157.
- Lifschitz & Lowrie, Z. wiss. Phot., 1917, 16, 269; C 1917, II, 357.
- Pfeiffer, An. 1911, 383, 109. Organische Molekulverbindungen.
- Reddelien, J. pr CH. 1915, 91, (2), 213.
- Rupe, An. 1890, 256.
- Posner, An. 1904, 336, 85.

Sachs & Barschall, B. 1901, 34, 3047.
Sachs & Lewin, B. 1902, 35, 3575.
Staudinger & Kon, An. 1911, 384, 121.
Stobbe, An. 1906, 349, 349.
Stobbe & Haertel, An. 1909, 370, 9399.
Straus, B. 1904, 37, 3277.
Thiele, An. 1899, 306, 87.
Vorlander, An. 1905, 341, 18, 19.
Werner, B. 1908, 41, 1062.
Witt, B. 1876, 9, 522; 1885, 18, 1119; 1886, 19, 441; 1888, 21, 325.
Zincke, An. 1904, 330, 361; 1904, 333, 296; 1905, 341, 365.
Zincke & Muhlhausen, B. 1903, 36, 134.

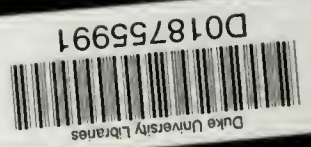
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Double-Conjugated Ketones

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